

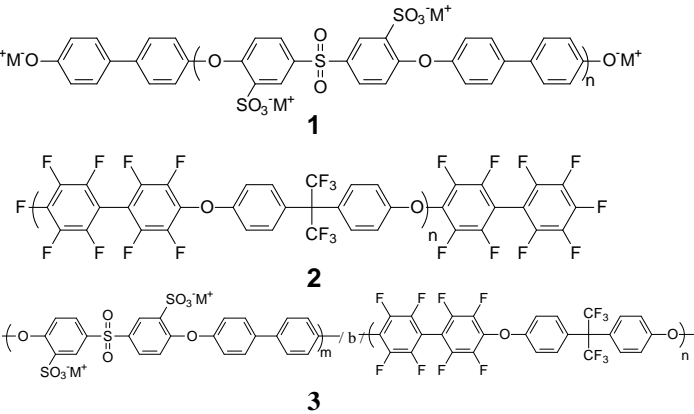
Evaluation of multiblock sulfonated-fluorinated poly(arylene ether)s membranes for a proton exchange membrane fuel cells (PEMFC): the role of phase morphology

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Proton exchange membrane fuel cells (PEMFCs) offer potential advantages of clean and efficient energy conversion systems for automobiles, portable applications, and power generation. Perfluorosulfonic acid polymer membranes, the best known example of which is DuPont’s Nafion®, are most widely used both in fuel cell research and industry. However, they suffer from several shortcomings among which their high cost presents a major obstacle for widespread application in fuel cell. In addition, a loss of proton conductivity above 80°C and low resistance toward alcohols cross-overs impose restrictions on the operating temperature and choice of possible fuels. These limitations have motivated many efforts in the development of alternative membrane materials based on sulfonated aromatic polymers.¹⁻⁶ In general, these polymers are expected to have lower production cost as well as satisfactory chemical and electrochemical stability for many applications.

In this paper we report evaluation of new proton exchange membranes as polymer electrolytes for a proton exchange membrane fuel cell (PEMFC). Sulfonated-fluorinated poly(arylene ether) multiblocks (MBs) were synthesized by nucleophilic aromatic substitution of fluorine-terminated telechelics made from decafluorobiphenyl and 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA) and hydroxyl-terminated telechelics made from biphenol and disulfonated dichloro-diphenylsulfone.

The MBs with various sulfonation levels were characterized using ¹⁹F, ¹H NMR, thermogravimetric analysis (TGA) and back titration. Their proton conductivity was measured as a function of relative humidity and temperature and was found to correlate with the water uptake of these materials. The data obtained from MBs was compared with commercial PEM Nafion®.



The multiblock copolymers **3** were prepared by the reaction of the dialkali metal salt of bisphenol-terminated disulfonated poly(arylene ether sulfone)s with decafluorobiphenyl-terminated poly(arylene ether)s in a polar aprotic solvent. The reaction was rapid and yielded copolymers with light yellow color. The dialkali metal salts of bisphenol-terminated disulfonated poly(arylene ether sulfone) **1** were generated using 3,3'-disulfonated-

4,4'-dichlorodiphenylsulfone and excess amount of biphenol in the presence of potassium carbonate at 160°C. Similarly, decafluorobiphenyl-terminated poly(arylene ether)s **2** were synthesized using 6F-BPA and excess amount of decafluorobiphenyl in DMAc-benzene mixed solvent.⁶

All the reactions produced high molecular weight copolymers in high yield. Films cast from solution were tested for ion exchange capacity by titrating with sodium hydroxide standard solution (Table 1). The multiblock copolymers had high water uptake both in salt and acid form. Conductivity of these materials in their fully hydrated form in liquid water showed values between 0.30-0.32 S/cm. Figure 1 displays the effect of relative humidity on proton conductivity for two MBs and Nafion 1135. As expected, the proton conductivity for both MBs and Nafion decreased exponentially as the relative humidity decreased. Both MBs exhibit higher proton conductivities than Nafion at low relative humidity. This surprising result may be attributed to the existence of nano-structure morphology forming sulfonated hydrophilic domains surrounded by fluorinated hydrophobic segments. Further investigation is underway on conductivity of MBs at high temperature and various levels of humidity.

Table 1. Characterization of multiblock copolymers

Sample	Block size (Kg/mol) ¹		IEC (meq/g) ²		Water Uptake (%)
	S	F	Calc.	Exp.	
MB-229	5	2.8	2.05	2.29	470
MB-210	5	2.8	2.05	2.10	360
MB-150	5	5	1.55	1.50	130
MB-117	5	5	1.55	1.17	115
MB-095	3.2	5.3	1.17	0.95	41
Nf-1135	-	-	-	0.89	38

(1) Target value, (S) represents the sulfonated block and (F) represents the fluorinated block. (2) Samples were acidified in 0.5 M boiling sulfuric acid for 2 h and boiling deionized water for 2 h.

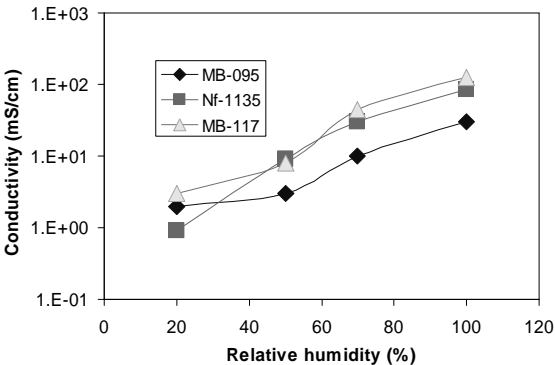


Figure 1. Influence of relative humidity on proton conductivity

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